

Semi-Annual Status Report

to

National Aeronautics and Space Administration

for

Research Grant NsG-247-62 to the Florida State University

FACILITY FORM 602	N65-87934	
	(ACCESSION NUMBER)	(THRU)
	5	None
	(PAGES)	(CODE)
	(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

by
Leo Mandelkern
Principal Investigator
August 1, 1965

The major research area of this program has been concerned with the fundamental acts of crosslinking polymers by high energy ionizing radiation and the dependence of the crosslinking efficiency and resulting network properties on the state of the system and the temperature at the time the crosslinks are introduced. The properties of polyethylene have received major attention and all quantitative studies have been limited to molecular weight fractions encompassing a wide range in molecular weights, crystallized under controlled conditions. The utilization of molecular weight fractions allows a more quantitative analysis to be made of the experimental results and the separation of effects due to crystallinity and temperature.

We have shown previously that when a comparison is made at 130°C between the irradiation of a highly crystalline and completely amorphous specimen of the same molecular weight, the crosslinking efficiency is greatly enhanced in the crystalline state. However, as the temperature is lowered below 90°C , the crosslinking efficiency in the crystalline state is drastically reduced. A major portion of the current research is directed to seeking an understanding of the relative changes in crosslinking efficiency through study of the radiochemical acts involved and structural changes that may occur within the crystal.

To this end studies of hydrogen evolution, formation of trans-vinylene groups, and vinyl decay have been studied as a function of radiation dose and temperature for molecular weight fractions covering the range 2,000 to 250,000. These samples and temperatures represent a wide range in the level of crystallinity, from being completely amorphous to being about 90% crystalline. A detailed quantitative mechanism has not as yet been formulated and developed. However,

certain salient features have evolved from the studies to date which will have to be given major consideration in the development of the mechanisms and the arrival at a material balance. One of the major problems encountered is that of properly accounting for the mechanism of vinyl decay since there appears to be one vinyl group per molecule. The initial G-value for vinyl decay is dependent not only on molecular weight and temperature but also on the state of the system at high temperatures. The G-value for the highly crystalline system is approximately twice that for the completely molten system at 133°C. On the other hand the G-values for trans-vinylene formation are only affected by temperature and phase in a minor way. The G-values for hydrogen evolution are only slightly sensitive to crystallinity content but are quite temperature dependent. Based on the previous crosslinking results difficulties can be anticipated in developing a simple material balance equation, until the mechanism of the vinyl decay and the possible utilization of hydrogen in this process is clarified. One approach currently being undertaken is to avoid this difficulty by working with very high molecular weight samples where the initial vinyl group concentration is negligible and assessing whether a material balance is obtained under these conditions. An unfractionated sample of linear polyethylene, $M_n = 7 \times 10^6$ has been obtained and preliminary studies are underway utilizing this material. It has already been confirmed that no significant chain scission processes occur during the irradiation of the completely amorphous polymer.

The concentrations of vinyl and trans-vinylene groups were measured by infra-red methods. Consequently appropriate extinction coefficients as a function of the degree of crystallinity had to be determined. As a by-product of this work, it has been demonstrated that at room temperature several

absorption bands can be utilized to measure the degree of crystallinity over a wide range in this quantity and that the results obtained correlate very well with other methods. The absorption coefficients of these bands as a function of temperature are now being studied to ascertain whether any molecular information can be obtained in regard to the effect of temperature on the increased crosslinking efficiency in the crystalline state. In particular we are interested in whether any modes of motion are enhanced in the crystalline regions above 90°C.

Previous analysis of the sol-gel curves of crystalline polyethylene irradiated at room temperature indicated the strong possibility that chain scission processes played an important role as compared to irradiation at elevated temperatures both for the crystalline and amorphous states. This possibility is being quantitatively investigated by measuring the changes in intrinsic viscosity as a function of dose of highly crystalline low molecular weight polyethylene in the pre-gelation region. This procedure has been adapted since more highly crystalline polymer can be obtained for lower molecular weights. The high doseages required for gelation precludes serious study in the post-gelation region. A quantitative analysis of the data obtained to date supports the concept that the ratio of chain scission to crosslinking substantially increases in highly crystalline polymer at room temperature compared to the same quantity at elevated temperatures.

The nuclear magnetic resonance studies, aimed at investigating the molecular motions within the crystal are continuing. The results with highly crystalline polymers give strong evidence for the onset of molecular motions within the crystalline regions at temperatures of about 90-100°C. The high quality of the spectra obtained with molecular weight fractions has necessitated a careful analysis and modification of the conventional instrumentation usually used.